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Fire-Retardant/Fire-Resistive Coatings

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Paint-type coatings can be divided into three general classes: conventional paints, varnishes, and enamels; fire-retardant coatings formulated with halogen compounds with or without special fillers; and intumescent coatings designed to foam upon application of heat or flame for development of an adherent fire-resistive cellular char.

99.1 Conventional Paints

Non-flame-retardant coatings usually give a low flame spread rating over asbestos-cement board, steel, or cement block. When the coatings are tested over wood and other flammable materials, flame spread ratings similar to those of the substrate are obtained.¹

The fire-retardant effectiveness of paints is highly dependent on the spreading rate or thickness of the coating as well as the composition. When conventional paints are applied at the heavy rate common for fire-retardant coatings, they give flame spread indices comparable to those of fire-retardant paints. For example, coating of latex and flat alkyd paints applied to tempered hardboard at an effective spreading rate of 250 ft²/gal reduced the flame spread index of the uncoated substrate by factors of 3 and 5, respectively.²

99.2 Fire-Retardant Paints

Fire-retardant coatings are particularly useful in marine applications. Ships are painted repeatedly to maintain maximum corrosion protection. As the layers of paint build, they pose a fire hazard even though the substrate is steel. In the event of fire, the paint may catch fire, melt, drip, and cause severe injury and damage to the vessel. Coatings are therefore formulated that do not sustain combustion; they should not spread the flame by rapid combustion nor contribute a significant amount of fuel to the fire.

Polyvinyl chloride containing 57% by weight chlorine is self-extinguishing. However, it is not a good vehicle for a flame-retardant coating because of its high melting point. This can be lowered substantially by copolymerization with other vinyl monomers such as vinyl acetate. To make these copolymers useful, addition of plasticizers and coalescing solvents is often necessary to give suitable application and per-

TABLE 99.1 Formulation for a Fire-Retardant Latex Paint

Ingredient	Parts by Weight
Polyvinyl acelate copolymer emulsion (55% solids)	20
Chlorinated paraffin	5
Antimony oxide	11
Titanium dioxide	22
Mica	9
Thickeners, etc.	3
Water	30

TABLE 99.2 Formulation for an Alkyd-Based Paint

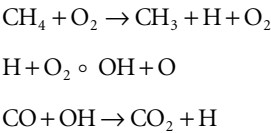
Ingredient	Parts by Weight
Long oil alkyd	22
Chlorinated paraffin	7
Antimony oxide	6
Titanium dioxide	29
Micronized talc	7
Whiting	11
White spirit drier, etc.	18

formance properties. These additions dilute the overall concentration of chlorine thereby reducing the flame retardancy.³

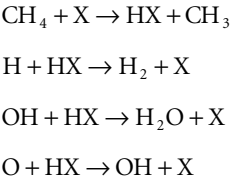
Fire-retardant coatings are based primarily on chlorinated alkyds, alumina trihydrate, or a combination of chlorinated paraffins and antimony trioxide. Table 99.1 and Table 99.2 give typical formulations. Flame spread test results depend both on the substrate and the thickness of the film.⁴

99.3 Fire-Retardation Mechanism

The combustion of gaseous fuel is believed to proceed by a free radical mechanism:



The H, OH, and O radicals are chain carriers and take part in a number of reactions in the flame zone. The function of halogen containing compounds as flame retardants has been explained by the radical trap theory and takes place in the gas phase. In the foregoing reactions, liberated HCl or HBr competes for the radical species that are critical for flame propagation:

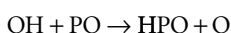
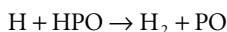
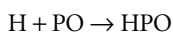


The active chain carriers are replaced with the much less active halogen radical, slowing the rate of energy production and helping flame extinguishments.

Antimony oxide is known as a flame-retardant synergist when used in combination with halogen compounds. Volatile antimony oxyhalide (SbOX) and/or antimony trihalide (SbX_3) form in the condensed phase and transport the halogen into the gas phase.

Phosphorus compounds are also used as primary flame retardants. The flame-retardant mechanism for phosphorus compounds varies with the type of compound, the polymer, and the combustion conditions.⁵ For example, some phosphorus compounds decompose to phosphoric acids and polyphosphates. A viscous surface glass forms and shields the substrate from the flame. If the phosphoric acid reacts with the polymer (e.g., to form a phosphate ester), subsequent decomposition results in a dense surface char. The coatings that form serve as a physical barrier to heat transfer from the flame to the substrate and to diffusion of gases; in other words, the substrate is isolated from heat, flame, and oxygen. This is the mechanism for fire-resistive intumescent coatings discussed below.

Triaryl phosphate esters are thermally stable, high boiling ($>350^\circ\text{C}$) materials. They can volatilize without significant decomposition into the flame zone, where they decompose. Flame inhibition reactions, similar to the halogen radical trap theory, have been proposed.⁶



Alumina trihydrate (ATH) or magnesium hydroxide inhibits ignition by absorption of heat due to decomposition, releasing large volumes of water of hydration ($>30\%$).

99.4 Fire-Resistive Intumescent Coatings

Intumescent paints and mastics swell and char when exposed to heat and flame, giving a carbonaceous foam that insulates the substrate from heat, air, and fire. This may delay the onset of combustion of a wood or plastic substrate or delay the heat buildup and tensile loss of structural steel. In the latter case, thick coatings or mastics are used. These coatings are considered to be fire resistive and significantly more effective than fire-retardant coatings. The former offer protection to the substrate. Intumescent coatings require three basic ingredients: a carbonific or carbon producer such as pentaerythritol or other polyol, an acid releasing agent such as a phosphate, and a spumific or gas producer such as melamine. Polyols such as starch and dipentaerythritol (less water sensitive) are carbonifics. Other acid producers and their temperatures of decomposition are ammonium polyphosphate (215°C), monoammonium phosphate (417°C), and melamine phosphate (300°C); spumifics include urea (130°C), dicyandiamide (210°C), and melamine (300°C).⁷

When the coating or mastic is heated, the decomposing phosphate forms phosphoric acid. This esterifies the hydroxyl groups of the polyol, which subsequently decomposes, forming water and a carbonaceous char, regenerating the phosphoric acid. As the char forms, the paint binder softens and the spumific decomposes, liberating nonflammable gases. These gases expand the softened binder into a foam. A rigid carbonaceous foam is formed as charring of both carbonific and binder resin is completed.

Table 99.3 and Table 99.4 give examples of intumescent systems.⁴

When used as a thick mastic coating on structural steel, such materials can prevent the steel from reaching the failure point for 3 hours, as indicated in Table 99.5.

A unique intumescent coating containing no water-sensitive polyols is composed of *p,p'*-oxybis(benzenesulfonamide) in a vinyl chloride–vinylidene chloride copolymer binder. The addition of melamine pyrophosphate improves the homogeneity of the system.⁹ Dipentaerythritol can also be added to improve the homogeneity.¹⁰

TABLE 99.3 Formulation for a Typical Intumescent Emulsion Paint

Ingredient	Parts by Weight
Polyvinyl acetate latex	18
Ammonium polyphosphate	22
Pentaerythritol	12
Starch	3
Dicyandiamide	16
Titanium dioxide	4
Water	25

TABLE 99.4 Formulation for a Typical Intumescent Solvent–Thinner Paint

Ingredient	Parts by Weight
Vinyl toluene–butadiene copolymer	7
Ammonium polyphosphate	28
Dipentaerythritol	8
Melamine	9
Chlorinated paraffin	9
Titanium dioxide	6
Mineral spirits	33

TABLE 99.5 Ratings on Steel Column

Coating Thickness (in)	Rating (h)
0.31	1
0.39	1.5
0.58	2
0.78	2.5
0.97	3

Source: From Seiner, J. A., and T. A. Ward, *Poly. Paint Colour J.*, 178(4207), 75–78 (February 10, 1988).

Pitt-Char (PPG Industries) coating is a two-component epoxy-polyamide produce designed for structural steel. This intumescent epoxy coating requires no reinforcement and provides up to 3 hours of fire protection.¹¹

99.5 Miscellaneous Coatings

Magnesium oxychloride mastics will protect steel by releasing large quantities of water upon heating and by relatively high temperature calcining (500°C). This material can be painted or sprayed and can be used in exterior applications.¹²

Polystyrene foam block can be protected against fire for specified time periods. Building plastics containing gypsum and perlite and an expanded vermiculite, Portland cement, and limestone coating are particularly effective in protecting polystyrene foam block against the heat of a simulated mine fire.¹³

For an insight into potential methods of flame retarding polyurethane and epoxy coatings, an analogy with plastic flame retardants can be made. The most common way to achieve flame-retardant polyurethanes is by the addition of halogen, phosphorus, chlorophosphate, or chlorophosphonate compounds. Reactive halogen and phosphorus diols have also been used. Epoxy resins are generally flame retarded using the reactive tetrabromobisphenol A. Use of phosphorus–halogen compounds has been reported.

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